Fuel Properties and Physicochemical Characterization of *Cannabis Sativa* Seed Oil

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Abstract **- Physicochemical and fuel properties of cannabis sativa seed oil (CNBSO) and its corresponding biodiesel (CNBB100) from transesterification reaction was investigated. The oil yield from Cannabis sativa seed was found to be 60% using n-hexane solvent and biodiesel yield of 78% was obtained when trans-esterified at 60 °C within few minutes of reaction time and oil to methanol ratio of 2:12 using NaOH as catalyst. Series of fatty acids were identified and quantified from the oil using GC-MS. The physicochemical properties of the oil as well as the corresponding biodiesel produced show a good correlation with the nature or type of fatty acids. The fuel properties of cannabis sativa compared favourably to that of fossil-based diesel. The reasonable oil yield and good fuel properties suggest that cannabis sativa seed oil is very useful for biofuel production which represents alternative use or value to the plant which many abused as drug.**

Keywords: **biodiesel, transesterification reaction, fatty acid, fuel properties, cannabis sativa seed oil**

I. INTRODUCTION

Largely all energy consumed in the world comes from fossil fuels (petroleum oil, coal and natural gas, etc). However, these sources are limited and will be exhausted in the near future [1], [2]-[3]. Biodiesel is a fuel that can replace diesel and it is made from renewable sources such as vegetable oils and animal fats. This fuel is biodegradable and non-toxic and has low profile pollutant emissions compared to petroleum diesel.

The use of biodiesel will allow the development of agriculture, economy and environment [4]-[5] Biodiesel is produced through a reaction known as transesterification were one mole of triglyceride is reacted with three moles of alcohol (molar ratio of methanol to 3:1 vegetable oil) to form one mole of glycerol and three moles of the respective fatty acid esters [6]-[7].

Various types of vegetable oils, with a varying composition in fatty acids, can be used for the production of biodiesel. The ideal vegetable oil for biodiesel must be readily available, its plant should be easy to cultivate and its composition must include a high percentage of mono-unsaturated fatty acids (C16:1, C18:1) [11]. Biodiesel is miscible in petroleum diesel. This means that the two can be mixed in any proportion and poured into the fuel tank. Common language for a biodiesel/diesel mix is "B" followed by the percentage of biodiesel. So, 20% biodiesel and 80% diesel are called B20 and B80 respectively. Pure biodiesel is called B100. The miscibility of biodiesel and petroleum diesel has advantage in the sense that users can choose to increase the proportion of petroleum diesel in the blend if they are discouraged by the slightly higher cost of biodiesel or cold weather operation problems encountered using high proportion of biodiesel. In very cold conditions, biodiesel begins to crystallize, becomes thicker and may be difficult to use in an engine. In that way one may use additives in the fuel, install any of a number of heating systems or use the biodiesel in a blend with petroleum diesel (which crystallizes) at a lower temperature [12].

Biodiesel can also be used in its pure form (B100), but may require certain engine modifications to avoid maintenance and performance problems. Due to it different properties, biodiesel will cause some changes in the engine's performance and emissions including lower power and emission of higher oxides of nitrogen. It can be blended in any proportion with petroleum-based diesel fuel and the impact of the changes is usually proportional to the fraction of biodiesel being used. These changes can be eliminated by the engines electronic control system by either injecting more fuel or adjusting the fuel injection timing if the proportion of the blend is known [37].

In contrast to palm oil, sugar cane, maize, etc., Cannabis is a highly adaptable, fast-growing, annual plant that can be cultivated at most latitudes. In addition, Cannabis is one of the few plants that produce high yields of both oil and biomass, which means it can be used to produce both biodiesel and bioethanol [10]. Consequently, Cannabis has the potential to form the basis of a revolutionary fuel industry and enhance some fossil activities [10]. Cannabis sativa can be grown even on "marginal" lands because it has low input requirements for cultivation. It can be efficiently used as a preceding crop for the cultivation of cereals since it increases their yields from 10-20%, is a pest-resistant, highly adaptable plant even in monoculture fields. It allows for a low pesticide use if followed by a well-designed crop rotation. it is an annual plant that fits well in crop rotations and it has the ability to suppress soil pathogens opening the path for a healthier soil [25].

The fossil diesel fuel is made up of a mixture of various hydrocarbon molecules and contains very little oxygen percentage (0.3%) but for the biofuels the amount of oxygen is about 10% of the fuel composition. The increase of oxygen in fuel structure results in reduction of carbon and hydrogen in the fuel and this will result in lower energy content [18]. Oxygen is ballast in fuel and carbon and hydrogen are source of thermal energy [18]. Presence of more oxygen can also cause lower stoichiometric air/fuel ratio. This can ensure improvement of combustion [18]-[19].

Not much Studies on the influence of the triglyceride composition on the biodiesel properties is available [8]. Investigation has shown that there is important relationship between triglyceride composition and the quality of biodiesel. Reference [24] reported high viscosity, density and cloud point of two biodiesel synthesized from soybean oil and beef tallow. The high cloud point of methyl esters of tallow biodiesel is indicative of a high concentration of saturated fatty acid esters. Reference [2] investigated the relationship between the oxidative stability of biodiesel from rapeseed oil and the percentage of linolenic acid. And reported that the higher the percentage of unsaturation the lower the oxidative stability. In related development, reference [7] studied transesterification of vegetable oils, comparing properties such as density, viscosity, cloud point and pour point and other differences established between them. The work reported that all the differences are as a result of saturation or unsaturation of the fatty acids. Another important parameter of a fuel is the calorific value, which represents the amount of heat transferred to the chamber during combustion and indicates the available energy in a fuel [4]. The higher the calorific value, the greater the energy contained in the fuel. The calorific value of biodiesel is higher (39-41 MJ / kg) compared to liquid fuels. It is lower than petrol (46 MJ / kg), diesel fuel (43 MJ kg-1) or oil (42 MJ / kg), but higher than coal (32-37 MJ kg-1) [9].

This study investigates the biofuel fuel potential of cannabis to be used as alternative fuel to fossil-based fuel in diesel engine. Fatty acids composition of the oil was characterized and correlated with the physicochemical properties and fuel properties of the corresponding biodiesel. The biodiesel was found to have good fuel properties that favourable compared with fossil-based fuel.

II. MATERIALS AND METHODS

Cannabis sativa seeds used for this study were obtained from Kasuwan Dare in Gwagwalada , Abuja FCT and identified in Medicinal Plant Research and Traditional Medicine Department (MPRTMD) of National Institute for Pharmaceutical Research (NIPRD), Idu. After which the seeds were dried for two weeks.

A. Extraction of Oil

The sample was grounded and packed into the extraction chamber of the Soxhlet extractor; n-hexane poured into the round bottom flask of the extractor; according to method 28.002 described by [14]. The whole set-up was mounted on a heating mantle at 65^{o}C and allowed to reflux for about 8 hours. The extract was evaporated using a rotary evaporator to isolate the free flow lipid from the solvent. The extracted oil was further evaporated in an oven at 150°C to eliminate any moisture and residue solvent that may be present. The weight of the oil produced and the residue were measured to ascertain the percentage of the oil content.

B. The Fuel Properties

Fuel properties such as flash point, viscosity, pour point, Specific gravity, Density, Calorific value, Oxidative stability, Cetane number, were characterized in accordance with the procedure outlined in [16].

C. GC-MS Analysis

The fatty acid composition of the oil samples was analysed using a Gas Chromatography Mass Spectrometer (GC-MS) of model: GCMS QP 2010, Shimadzu, Japan. It is equipped with capillary column (Optima 5MS Length 30m, 0.25mm I.D, 0.25µm thickness) and He as the carrier gas. at the initial temperature of 60^{o}C and injection temperature of 250^{o}C. The analysis of the sample was carried out by injecting 1µl of the extracted oil into the GC. The identification of the fatty acid was achieved by library search (NIST08 LIB).

D. Physicochemical Analysis

The physicochemical properties (Refractive index, specific gravity, colour, Iodine value, saponification value, acid value, free fatty acid value) were determined using standard procedures [14]-[17].

E. Determination of Percentage (%) Oil Yield of CNBSO

The percentage (%) yield was calculated using the equation (1)

$$\% \text{ yield of oil} = \frac{\text{weight of oil}}{\text{Weight of sample}} \times 100$$

III. RESULTS AND DISCUSSION

A. Fatty Acid Composition

The fatty acid composition of biodiesel has a key role in the physical and chemical properties of fuel. The performance of an ester (biodiesel) as diesel fuel depends on the chemical composition of the ester, particularly on the length of carbon chain and the degree of saturation and unsaturation of fatty acid molecules [18]. Studies show that properties such as cetane number, cold flow characteristics and oxidation stability are affected by the fatty acid composition [19]-[20]. There are three main types of fatty acids including saturated, unsaturated and polyunsaturated. Vegetable oils with higher degree of unsaturation tend to have higher freezing point, poor flow characteristic and can become solid [19].

The Fatty acid profile of cannabis sativa seed oil extracted and methyl ester biodiesel (CNBB100) produced are presented in table i and ii respectively. The results showed that the seed oil contains fatty acids namely: Oleic (24.78 ± 1.30 %), stearic acid (20.34 ± 1.50 %), palmitic (11.86 ± 1.60 %), and Eicosanoic acid (0.80 ± 1.30), while that of the fuel are: Linoleic acid methyl esther (53.67 ± 1.34 %), stearic acidme (14.07 ± 1.43 %) and palmitic me(13.90 ± 1.58 %). The difference in fatty acid profile in the raw oil and biodiesel is due to the derivatization that occurs during transesterification of the biodiesel produced as FAMEs content is high, due to derivatization. The raw oil contains quite low quantity of FFA (https://www.sciencedirect.com/topics/food-science/free-fatty-acids) while remaining fatty acids are present as triacylglyceride (TAG-bound). During trans-esterification reaction, all these fatty acids (FFA + TAG bound) gets converted to FAME in the biodiesel leading to high fatty acid profile as compared to the lower FFA content in the raw oil.

TABLE I FATTY ACID OF **CNBSO**

Fatty Acids	Area % composition
Palmitioleic acid	9.21
Palmitic acid	2.65
Oleic acid	24.78
Stearic acid	20.34
Eicosanoic acid	0.80

TABLE II **FATTY** ACIDS OF **CNBB100**

Fatty Acids	**Area % composition**
Decanoic acid methyl ester (C11)	0.14
Myristic acid methyl ester (15)	0.22
Palmitic acid, methyl ester (C17)	13.90
Palmitoleic acid, methyl ester (C17)	0.95
Oleic acid methyl ester (C19)	14.05
Linoleic acid methyl ester (C19)	53.67
Stearic acid, methyl ester (C19)	14.07
Capric acid methyl ester (C 19)	0.10
Eicosanoic acid, methyl ester (C21)	0.22
Behenic acid methyl ester (C23)	1.76
Total	99.08

TABLE III PHYSICOCHEMICAL PROPERTIES OF **CNBSO**

S/N	**Analysis**	**Results**
1	Colour	Dark Brownish
2	Texture at 37^oC	Liquid
3	Odour	Agreeable
4	Specific gravity g/ml @ 40^oC	0.949
5	Refractive index @ 24.8^oC	1.463
6	moisture content (%)	0.2
7	Iodine value (g/100g)	68.31
8	Saponification value KOH/g	185.56
9	Acid value mgKOH/g	11.781
10	Free fatty acid mgKOH/g	5.891
11	Viscosity mm^2s^{-1} @40^oC	90.4
12	Density gm^{-1} @40^oC	0.94
13	Carbon Residue	0.1
14	Calorific value MJ / kg	42.789

B. Physicochemical Properties

The Physicochemical properties of the oil presented on table iii; refractive index was found to be 1.463 ± 1.33. This showed that the oil is less thick and comparable with most oils whose refractive indices are between 1.475 and 1.485 [21]. The refractive index value also showed that the oil contained some double bonds in its fatty acid composition [22]. It is reported that the refractive index increases as the double bond increases [22]. This indicates that the seeds oil analysed have a high proportion of unsaturated fatty acids (agreeing with the refractive index value) and suggests that the seed oil could be useful in the production of biodiesel.

I. Iodine Value

The iodine value is a measure of unsaturation of fats and oils [20]. Iodine value is expressed in terms of number of centigrams of iodine absorbed per gram sample of biodiesel. The iodine introduced into the biodiesel reacts with the double bonds within the fatty acid structure. Therefore, the higher the percentage of unsaturation, the larger will be the iodine value [18]. The iodine numbers can influence oxidation stability and the polymerization of glycerides. This can lead to the formation of deposits formed in diesel engines injectors [26]-[6]. The results of iodine value test are shown in table iii. This can be a good indication of unsaturation of cannabis biodiesel. The unsaturation of fuel can have significant effects on several chemical and physical properties of fuels. Based on the results of Iodine value, this is an indication for higher unsaturation of CNBB100.

II. Calorific Value

Calorific value is defined as the energy contained in a fuel, determined by measuring the heat produced by the complete combustion of a specified quantity of it. Calorific value is an important parameter in the selection of a fuel. The fuel elements of primary interest to diesel engine combustion are carbon, hydrogen, oxygen and sulfur and the calorific value of a fuel is directly related to its elemental composition [18]. Calorific value of fuel increase with chain length of molecule [36]. The highest calorific value belongs to fossil diesel (45.8 MJ/kg). The calorific value of CNBB100 is 37.986 MJ/kg. The lower calorific value as compared to fossil diesel is due to the higher oxygen content of the biofuels [19]-[27].

III. Acid Value

Acid value is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acid presents in 1 gram of the sample. Acid value can also be an indication of lubricity degradation [28]. Higher acid value can cause fuel system deposits and reduces the lifelong of fuel pump [26]. The results of acid value analysis are shown in table iii. The acid value of CNBB100 is 11.781mg of KOH and the acid value for fossil diesel is 0.015 mg of KOH which is lower; hence it has the tendency to form less deposits and low lubricity degradation. The main reason for this trend can be due to unsaturation level of the CNBB100, as cannabis has higher unsaturation. Hence, the unsaturated fatty acid with double bonded long chain hydrocarbons has more susceptibility to oxidation and oxidation has an inverse relation with acid value [29]. Increase of acid value can be considered as a result of oxidation of the fuel which may lead to gum and sludge formation besides corrosion [19]. Temperature can also affect the acid value. If fuel is exposed to high temperature oxidation occurs due to higher rate of reaction of fuel molecules with oxygen in the air, result.ng in increase of acid value [29].

IV. Density

The density of biofuels is one of the main concerns in widely utilization of them. Density is defined as the ratio of mass per unit of volume of an object. The higher the density, the tighter the particles are packed in the substance. Fuel injection devices work on a volumetric system, hence a higher density for biodiesels results in delivery of slightly greater mass of fuel into combustion chamber. The higher density of biodiesels can also cause more particulate matter (PM) production due to deterioration of fuel atomization [30]-[18]. The results of density test as shown in table iv shows CNBB100 is higher (0.89 g/cm3) than fossil (0.88 g/cm3) though the difference is not so much. This trend can be connected to saturation level of fatty acids present in CNBB100. Saturation of fatty acids can increase the density. Since the fuels containing shorter chain length of hydrocarbon have more saturated fatty acids, they are more prone to be crystallization and therefore may cause reduction of its volume and consequently increase of density [29]. The density also is affected by oxidation of fuel. The density has direct relation with fuels molecular weight; thus, oxidation of fuels can increase the mass of fuel by producing by products and sediment, and therefore it results in increase of density [29]. The density of CNBB100 therefore indicates that its particles are tighter and can be used in fuel injector devices. Cannabis biodiesel compares favourably with fossil fuel.

V. Viscosity

Viscosity is defined as the resistance of a liquid to flow. Viscosity can be considered as one of the main obstacles in widely usages of biodiesel fuels. In the fuels with higher viscosity, engine durability is the main concern. Fuel with higher viscosity can cause soot deposit formation on injectors (injector clogging), certain components of piston (rings), inlet and outlet valves and fuel filter plugging [31]-[32]. The higher amount of biodiesel concentration partly dissolves the lubricant, resulting in increased friction of engine moving parts [31]. Fuel atomization and volatility is also affected by viscosity. Higher viscosity results in poorer fuel atomization which leads to combustion deterioration [31], [29], [18]-[26]. The higher viscosity can also make low temperature flow problems and cold engine start up and ignition delay [26]-[28]. The results of viscosity test are shown in table iv. The viscosity values of biodiesel are higher than fossil diesel. This can be due to the difference of molecular composition of the samples and the level of unsaturation of CNBB100. As the proportion of saturated fatty acids with longer carbon chain increases, it can increase the viscosity [26]-[30]. Thus, for cannabis with higher percentage of unsaturated components (about 45.33%) can show higher viscosity in comparison with fossil diesel. Oxidation stability of fuels is another important parameter.

TABLE IV PHYSICOCHEMICAL PROPERTIES OF **CNBS**

Fuel Properties	**CNBB100**	**Diesel (D2)**	**ASTM standard D6751**
Specific gravity	0.889	0.88	0.82
Flash point (°C)	115	70	100
Cloud point(°C)	8	2.0	-5.0
Pour point(°C)	-4	-2.0	-3.0
Viscosity(mm^2s^{-1})	4.76	240.22	1.9 – 6.0
Density (gml^{-1})	0.89	0.88	0.86
Calorific value MJ/Kg	37.986	43	-
Oxidative stability @110°C	321mins	360mins	EN 14112 3 min, hr
Cetane number	47.43	46	47
Copper corrosion	2b Moderately tarnished		
Carbon residue (%)	0.049	0.17	0.05max

C. Fuel Properties

The results in table IV shows the quality parameters of the produced biodiesel as compared to conventional diesel with ASTM D6751 as standard.

I. Cloud Point

The cloud point is an important feature of fuels in winter application. The cloud point is defined as the temperature at which crystals first starts to form in the fuel. The saturation of fatty acids increases the cloud point [19]-[26]. The cloud point is most commonly used as a measure of low-temperature operability of the fuels [33]. The cloud point of biofuels typically higher than the cloud point of conventional diesel [33]. The results of cloud point test are shown in table iv. Among the samples CNBB100 is (8 °C). The cloud point is an important feature of fuels in winter application. The cloud point of CNBB100 indicates it may crystallize faster than fossil diesel, this is due to higher saturation of fatty acids present in the biodiesel produced.

II. Oxidation Stability

The oxidation stability of fuels is an important element which can help to determine the quality of fuel and it can also affect some of fuel physical and chemical properties such as density, viscosity and water content. Biodiesels usually have 10% more oxygen in their structure which can increase the risk of oxidation. The fuel composition can also affect the oxidation stability. Studies show that vegetable oils which are rich in poly unsaturated acids tend to give methyl ester fuels poor oxidation stability [20],[26]-[32]. Oxidation occurs in the forms of aldehydes, alcohols, carboxylic acids, insoluble gum and sediments in biodiesel [29]. The temperature also has a great impact on oxidation rate. The thermal oxidation is determined by the rate of oxidation reaction at high temperature when the fuel is exposed to air and as the temperature increase the rate of oxidation increases [29]. Oxidation stability cannot be prevented entirely but can be delayed by application antioxidant [29]. The induction period (IP) of CNBB100 (321mins) lesser than fossil diesel (360mins) which is significantly higher. This can be due to various percentages of unsaturated fatty acids in biodiesel [29]. cannabis biodiesel has higher amount of linoleic acid, which is an unsaturated fatty acid this contributed to the low oxidation stability of CNBB100.

III. Flash Point

Flash point is another important property of any fuel. It is defined as the temperature at which a fuel can provide a combustible mixture with air while exposed to flame or spark. Flash point has an inverse relation with fuel's volatility [28]. Flash point is an important factor to consider in handling, storage and safety of fuels [34]. The results of flash point test are shown in table iv. The lowest flash point is for fossil diesel (70 °C) and highest belong to CNBB100 (115 °C). This ensures the safety of biofuels. The reason for this trend can be related to the fuel composition of the biodiesel sample. Diesel consists of hundreds of different hydro carbon components but biofuels are usually consisting of 4 to 5 major components that will boil at the same temperature [29]. Flash point can also decrease by oxidation and storage time [29].

IV. Pour Point

Pour point is the lowest temperature that the fuel is observed to flow. Pour point is an important property in winter use. Biodiesel exhibits poor flow properties at low temperature [35]. The structural properties of biodiesel that can affect the pour point are degree of unsaturation, chain length and degree of branching [35]. The results of the pour point test are shown in table iv. CNBB100 (-4 °C) fossil diesel has the lowest value (−20 °C) which can cope with cold climate flow problems where biodiesel may not. The higher level of saturation increases the pour point [26]-[35].

IV. CONCLUSIONS

The biodiesel produced (CNBB100) meet the ASTM D6751 standards for all tested parameters. The fatty acid structure of biodiesel impacted the oxidation stability of the fuel. This is mainly due to the level of saturation of the biodiesel. The fuel properties of CNBB100 determined indicates its fitness as a biodiesel, as most of the fuel properties specifications were closed to that of diesel D2 that was used as a standard.

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